Construction of Gas Transport Theory in Porous Media for the Entire Range of Knudsen Numbers

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論 文 内 容 要 旨

Chapter 1: Introduction

Gas transport through porous media has been used for various engineering devices for catalytic reaction, reductive reaction, drying and adsorption, because porous media have a large internal surface area which facilitates surface reactions. It is important to understand transport phenomena in porous media to improve the performance of such devices. Gas transport mechanism in porous media depends on the Knudsen number, which is defined as the ratio of the mean free path for intermolecular collisions of gas molecules to the pore size. In the case where the pore size of a porous medium is much larger than the mean free path for intermolecular collisions of gas molecules, i.e., in the case where the Knudsen number Kn is much smaller than unity, the gas flow through such a porous medium can be considered as a viscous continuum flow. On the other hand, in the case where the pore size of a porous medium is much smaller than the mean free path for intermolecular collisions of gas molecules, i.e., in the case where the Knudsen number is much larger than unity, the gas flow through such a porous medium is in the free molecular flow regime. In such a high Knudsen number regime, the Knudsen diffusion is the dominant transport mechanism of gas molecules through a porous medium. In the case where the pore size is comparable with the mean free path for intermolecular collisions of gas molecules, the gas flow through such a porous medium is in the transition flow regime, and hence, contributions of both Knudsen diffusion and viscous flow appear, making the problem difficult to understand. Therefore, the gas transport theory applicable to the entire range of Knudsen number has been required to clearly understand molecular transport through porous media.

Chapter 2: Construction of Theoretical Expression for Gas Transport in Micro- /Nanoscale Porous Media

In this chapter, porous media were represented by randomly arranged solid spherical particles with interpenetration of particles and pressure-driven gas flow through the porous media was simulated by using the direct simulation Monte Carlo (DSMC) method based on the Boltzmann equation. DSMC simulations were performed for different porosities and different sizes of solid particles of porous media. It was confirmed that Darcy's law holds even in the case for micro/nanoscale pores. Furthermore, we regarded a porous medium as a bundle of tortuous circular capillary tubes, and then theoretically constructed expressions to estimate pressure-driven gas flow velocity through porous media with pores from nanoscale to microscale and porosity ranging from 0.3 to 0.5 by superposing both contributions of Knudsen diffusion and viscous flow with a velocity slip. The flow velocities estimated by using the constructed expressions agreed well with those obtained in the DSMC simulations. From the proposed expressions for flow velocity U, we also obtained the theoretical expressions that show the effect of Knudsen number on superficial velocity U_s, i.e., volume flux, permeability K and Klinkenberg coefficient b of porous media. The equations proposed here are summarized as follows:

Knudsen-type of Kawagoe-Yonemura expressions for porous media:

$$U = -\tau\left(\frac{1}{3}\lambda_{\mathrm{wall}}\bar{C}\frac{1+c_1^{\mathrm{K}}p}{1+c_2^{\mathrm{K}}p}+\frac{\lambda_{\mathrm{wall}}^2}{32\mu}p\right)\frac{1}{p}\frac{\mathrm{d}p}{\mathrm{d}x}, \qquad b = \frac{128}{3\pi}\cdot\frac{1+c_1^{\mathrm{K}}p}{1+c_2^{\mathrm{K}}p}\mathrm{Kn}\cdot p,$$

$$U_{\mathrm{s}} = -\varepsilon\tau\frac{\lambda_{\mathrm{wall}}^2}{32}\left(1+\frac{128}{3\pi}\mathrm{Kn}\frac{1+c_1^{\mathrm{K}}p}{1+c_2^{\mathrm{K}}p}\right)\frac{1}{\mu}\frac{\mathrm{d}p}{\mathrm{d}x}, \qquad c_1^{\mathrm{K}} = 2.00\left(\frac{8}{\pi}\right)^{1/2}\left(\frac{\lambda_{\mathrm{wall}}}{2\mu\bar{C}}\right),$$

$$K = K_0\left(1+\frac{128}{3\pi}\mathrm{Kn}\frac{1+c_1^{\mathrm{K}}p}{1+c_2^{\mathrm{K}}p}\right), \qquad c_2^{\mathrm{K}} = 2.47\left(\frac{8}{\pi}\right)^{1/2}\left(\frac{\lambda_{\mathrm{wall}}}{2\mu\bar{C}}\right).$$

Wakao-type of Kawagoe-Yonemura expressions for porous media:

$$U = -\tau\frac{\lambda_{\mathrm{wall}}^2}{32\mu}\left[\phi\frac{128}{3\pi}\mathrm{Kn}+(1-\phi)\left\{1+\left(a+\frac{32}{3}\right)\mathrm{Kn}\right\}\right]\frac{\mathrm{d}p}{\mathrm{d}x}, \qquad b = \left[\phi\frac{128}{3\pi}+(1-\phi)\left(a+\frac{32}{3}-1\right)\right]\mathrm{Kn}\cdot p,$$

$$U_{\mathrm{s}} = -\varepsilon\tau\frac{\lambda_{\mathrm{wall}}^2}{32}\left[\phi\frac{128}{3\pi}\mathrm{Kn}+(1-\phi)\left\{1+\left(a+\frac{32}{3}\right)\mathrm{Kn}\right\}\right]\frac{1}{\mu}\frac{\mathrm{d}p}{\mathrm{d}x}, \qquad \phi = \frac{\mathrm{Kn}}{\mathrm{Kn}+1}.$$

$$K = K_0\left[\phi\frac{128}{3\pi}\mathrm{Kn}+(1-\phi)\left\{1+\left(a+\frac{32}{3}\right)\mathrm{Kn}\right\}\right],$$

where ε is the porosity of the porous medium, τ is the tortuosity of the porous medium, μ is the gas viscosity, p is the gas pressure, a is the rarefaction parameter which reflects the effect of gas rarefaction on gas viscosity, $\bar{C}$ is the mean molecular speed, λ_{wall} is the mean free path for molecule-wall collisions, i.e., the average distance traveled by a gas molecule between successive molecule-wall collisions, the Knudsen number Kn is given by $\mathrm{Kn} = \lambda_{\mathrm{mol}}/\lambda_{\mathrm{wall}}$ by regarding λ_{wall}

as the diameter of the tortuous tubes, λ_{mol} is the mean free path for intermolecular collisions, and K_0 represents the permeability in the continuum limit and is given by $K_0 = \varepsilon\tau\left(\lambda_{wall}^2/32\right)$.

Chapter 3: Investigation of Validity of Kawagoe-Yonemura Expressions to Different Type of Porous Media

In this chapter, we investigated whether the proposed expressions provide a good estimate of gas flow rate for any porous medium, whose internal structure is different from randomly arranged solid spherical particles. In the present study, a packed bed of spherical particles without interpenetration of particles was chosen as a different type of porous medium. It was found that when the tortuosity obtained for the randomly arranged solid spherical particles was used, our expressions underestimated the gas flow rate through the packed bed. However, when the tortuosity corresponding to the packed bed was used, the gas flow rates estimated by our expressions agreed well with those obtained in the DSMC simulations. These results suggest that a different internal structure of porous medium affects only the tortuosity in our expressions. Thus, even if a porous medium has a different internal structure from that considered in this study, our expressions may still give a good estimate of the gas flow rate by using the proper tortuosity corresponding to the porous medium.

Chapter 4: Investigation of Tortuosity of Porous Media with Nanoscale Pores Based on Paths of Moving Gas Molecules

In this chapter, the nature of tortuosity of porous medium was investigated. Tortuosity is one of the most important factors for porous medium because it determines fluid transport properties through the medium, and many tortuosity models have been proposed by empirical, analytical, and numerical approaches. As mentioned above, we constructed expressions to estimate pressure-driven gas flow rate through porous media with pores from nanoscale to microscale by regarding a porous medium as a bundle of tortuous circular capillary tubes. However, to provide a good estimate by using our expressions, the proper tortuosity corresponding to the porous medium is required. In order to evaluate the tortuosity properly, clear understanding of the meaning of the tortuosity is necessary. In the present study, we investigated the nature of tortuosity of porous medium by considering molecular paths of which gas molecules pass through it due to Knudsen diffusion. Before considering molecular paths in porous medium, we investigated molecular paths in a straight cylindrical tube in the case when intermolecular collisions are negligible. By performing numerical simulations of molecular motions in a straight cylindrical tube with diffuse reflection model for molecule-wall collisions, it was found that the ensemble average of the total path traveled by molecule until it is displaced with a certain distance is proportional to the square of the required displacement. This characteristic of the ensemble average of the total path of molecule was explained by considering the molecular motions in a straight cylindrical tube as a one-dimensional random walk. Based on this characteristic, we found that the tortuosity of porous medium can be expressed as the ratio of the average of total path traveled by molecule for a certain displacement in a straight cylindrical tube corresponding to porous medium to the average of total path traveled by molecule for the same displacement in the porous

medium. Using the tortuosity estimated by this, our expressions provided a good estimate of gas flow rate for porosities less than 0.5 over the whole range of Knudsen numbers considered here.

Chapter 5: General Conclusion

In this thesis, gas transport due to the pressure gradient through porous media was investigated by numerical and theoretical method, and the theoretical expressions to estimate gas transport through porous media regardless of the Knudsen number, i.e., regardless of the pore size, were constructed. Using proposed expressions, the permeability influenced by the rarefaction effect due to the smallness of pores can be determined from the liquid permeability, which can be easily measured in experiments. These expressions will help researchers and engineers to better understand the gas transport through porous media.

論文審査結果の要旨

多孔質体は，その比表面積の大きさから，触媒反応，乾燥，吸着，還元反応などの種々の工業プロセスで用いられる重要な材料であり，近年ではナノスケールの空孔をもつ多孔質材料が燃料電池の電極などに用いられるようになっている。気体の場合，空孔サイズが分子の平均自由行程程度まで小さくなると速度すべりなどの希薄気体効果が現れ，さらに小さくなると，ランダムな壁面衝突によるクヌッセン拡散現象が分子輸送の主たるメカニズムとなる。そのような多孔質体内気体流れに対しては，従来の連続体的な理論に基づく圧力損失と流量の間の関係式が適用できない。本研究は，多孔質体内の気体流れを数値シミュレーションにより再現し，分子運動と流体力学の視点から流動現象を考察することによって，あらゆるクヌッセン数領域で適用可能な多孔質体内の気体輸送理論を構築することを目的としている。本論文は，これらの成果をまとめたものであり，全編５章からなる。

第１章は序論であり，本研究の背景と目的，および論文の構成を述べている。

第２章では，重なりを許してランダムに配置した固体粒子群を多孔質体と見立てて，圧力勾配により誘起される気体流れを数値シミュレーションによって再現し解析するとともに，あらゆるクヌッセン数領域で適用可能な流量と圧力勾配の関係式を理論的に構築している。本理論式は，多孔質体内の複雑な流路を曲がりくねった円管の束と見なし，圧力勾配によって多孔質体内に誘起される気体流れの流量と圧力勾配の関係を記述している。その際に，低クヌッセン数で支配的となる粘性流れと高クヌッセン数で支配的となるクヌッセン拡散，および中間のクヌッセン数領域で顕著な速度すべりの効果を重ね合わせることにより，あらゆるクヌッセン数領域で適用可能な関係式を構築している。同時に，クヌッセン数依存性を考慮した透過率の式も導いている。これらの理論式を用いて見積られた流量は数値シミュレーションによって得られた流量と，空隙率が 0.3〜0.5 の範囲でよく一致している。また，ダルシーの法則がナノスケールの多孔質体に対しても成り立つことを数値シミュレーションにより確かめている。ここで得られた理論式および計算結果は多孔質体内の気体流動特性を表す重要な基礎的知見である。

第３章では，第２章で提案された理論式が内部構造の異なる多孔質体に適用可能かどうかを調べている。本章では，第２章と内部構造が異なる，粒子の重なりを許さない粒子充填層において，圧力勾配により誘起される気体流れの数値シミュレーションを行い，得られた流量と理論式により見積られた流量を比較している。その結果，多孔質体の内部構造に対応する迷路度を採用することにより理論式が良い見積りを与えることを明らかにしている。また，粘性係数に現れる希薄気体効果を表すパラメータの値も評価し，これを理論式に組み込んでいる。これらの結果は，本理論式の広い適用性を示す有用な知見である。

第４章は，多孔質体の迷路度が意味するところを分子運動の観点から分析している。本理論式において，多孔質体の迷路度は多孔質体の直線距離と多孔質体内部の曲がりくねった流路の長さの比の自乗で定義されている。しかし，高クヌッセン数領域において気体分子の移動経路は流線に沿わないため，多孔質体内の流路長さの意味合いが不明瞭であった。そこで本章では，円管内における分子のクヌッセン拡散による挙動と多孔質体内におけるクヌッセン拡散による分子の挙動を比較分析し，多孔質体の迷路度の意味について考察している。その結果，円管と多孔質体のそれぞれにおいて一定の直線距離移動するために分子が描く全行程の長さの比が多孔質体内流路の迷路度を表すことを明らかにしている。この知見は本理論式の物理的意味を明確にする重要な知見である。

第５章は結論である。

以上要するに本論文は，あらゆるクヌッセン数領域において適用可能な多孔質体における流量と圧力勾配の関係式を構築し，その妥当性および適用可能性を確かめたものであり，ナノメカニクスおよび分子流体力学の発展に寄与するところが少なくない。

よって，本論文は博士(工学)の学位論文として合格と認める。